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Sunflower Oil Hydrodeoxygenation in the Presence of NiMoS/B_2O_3–Al_2O_3 Catalysts

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Abstract—It has been shown that borate-containing alumina can be used as a support for sunflower oil hydrodeoxygenation catalysts at 380°C, 4.0 MPa, and a feed space velocity of 1 h^{-1} with a liquid product yield of 81–85 wt %. It has been found that, with an increase in the boron oxide content in the catalyst, owing to an increase in the catalyst acidity, the fraction of isoalkanes in the products increases to 77–78% and the contribution of decarboxylation/decarbonylation reactions to the formation of the products increases.

Keywords: hydrodeoxygenation, vegetable oil, sulfide catalysts, borate-containing alumina

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The increase in the fraction of low-grade oil in the total refining output, along with the simultaneous tightening of environmental standards, necessitates the search for new sources of feedstocks for the production of motor fuels. Biomass, the main advantage of which is rapid renewability, is thought of as a promising source of the feedstocks. It is believed that the use of biomass to produce fuels significantly mitigates the impact of greenhouse gases formed during fuel combustion on the climatic changes [1].

Fats, as a biomass component comprising C_{15}–C_{18} hydrocarbon (HC) moieties, are most promising for the production of diesel fuels (DFs). Second-generation biodiesel fuels are produced by hydrotreating fat-and-oil feedstocks. The absence of oxygen-, nitrogen-, and sulfur-containing compounds; unsaturated and polyaromatic HCs; and high cetane numbers provide high performance and environmental characteristics of these fuels compared with the characteristics of not only conventional diesel, but also first-generation biodiesel fuels, namely, fatty acid methyl esters.

The currently available industrial technologies for diesel production from fat-and-oil feedstocks have been developed by a number of foreign companies, such as Neste Oil (Finland) [2], UOP/Eni (United States, Italy) [3], Syntroleum (United States) [4], ConocoPhillips (United States, Ireland) [5], PETROBRAS (Brazil) [6], Haldor Topsøe (Denmark) [7], Nippon Oil (Japan) [8], and SK Energy (South Korea) [9]. Most of these processes are based on the use of modified hydrotreating schemes and conventional hydrotreating catalysts; in some cases, the feedstock is subjected to preliminary hydrogenation [10]. The resulting products are mixtures of C_{15}–C_{18} HCs with a high content of *n*-alkanes, the main disadvantage of which is a high pour point, which makes them inappropriate for use as winter DF components [11]. To improve the low-temperature characteristics, these components are additionally subjected to isomerization dewaxing in the presence of zeolite-containing catalysts [2, 10, 12, 13]. The use of a two-stage conversion scheme leads to a significant increase in the process costs and a decrease in the liquid product yield.

Attempts to implement the hydrodeoxygenation of a fat-and-oil feedstock and the isomerization of the resulting *n*-alkanes using a single bifunctional catalyst have been the focus of a large number of studies. These catalysts contain metallic, oxide, or sulfide hydrogenating components supported on acidic substrates, the properties of which determine the isomeric composition and, accordingly, the pour point of the resulting products. The most thoroughly studied acidic components of the catalysts are materials containing zeolites of various types, such as SAPO-11 [14–16], SAPO-31 [17], MSM-41 [18], SBA-15 [19], HY [20], Beta [21], and ZSM-22 [16]. In some reports, the use of anion-modified metal oxides is described: WO_x/Al_2O_3 [22, 23] or $Ce_{0.6}Zr_{0.4}O_2$ [24].

In this study, a nickel–molybdenum sulfide catalyst supported on a B_2O_3–Al_2O_3 (BA) acidic substrate of varying composition is tested as a catalyst for the hydrodeoxygenation of sunflower oil and the isomerization of the resulting alkanes. The main aim is to study the effect of boron oxide content in the catalyst on the hydrodeoxygenation process parameters and the product composition.

Table 1. Chemical composition of the catalysts

Sample	Element content, wt %					
	nominal			actual		
	Ni	Mo	B_2O_3	Ni	Mo	B_2O_3
NiMo/BA-0	3.6	12.0	0.0	3.7 ± 0.2	12.1 ± 0.6	0.0
NiMo/BA-5	3.6	12.0	5.0	3.8 ± 0.1	12.2 ± 0.4	5.1 ± 0.1
NiMo/BA-10	3.6	12.0	10.0	3.7 ± 0.1	12.1 ± 0.1	9.9 ± 0.4
NiMo/BA-15	3.6	12.0	15.0	3.6 ± 0.1	11.9 ± 0.2	15.3 ± 0.7
NiMo/BA-20	3.6	12.0	20.0	3.7 ± 0.1	12.2 ± 0.1	19.8 ± 0.3
NiMo/BA-25	3.6	12.0	25.0	3.7 ± 0.2	12.2 ± 0.2	25.0 ± 0.2
NiMo/BA-30	3.6	12.0	30.0	3.9 ± 0.2	12.6 ± 0.5	28.7 ± 0.9

EXPERIMENTAL

Catalyst Synthesis and Investigation Procedures

Borate-containing BA supports were synthesized by mixing commercial pseudoboehmite (Promyshlennye Katalizatory, Ryazan, Russia) with aqueous solutions of boric acid (analytical grade) and subsequently drying (120°C, 12 h) and calcining (550°C, 16 h) the resulting mixture [25]. The nominal boron oxide content in the catalysts was varied in a range of 5–30 wt % (samples BA-5—BA-30) by using boric acid solutions of different concentrations.

Nickel and molybdenum were introduced into the catalyst by the impregnation of the synthesized support (0.2–0.5 mm fraction) with solutions of bimetallic citrate complexes of nickel and molybdenum in a vacuum. The impregnating solutions were prepared using citric acid (GOST 908-04, Reakhim), $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (TsT Lantan), and $Ni(CH_3COO)_2 \cdot 4H_2O$ (reagent grade, Reakhim). Upon the completion of impregnation, the samples were dried at 220°C for 2 h. The molar ratio of metals—Ni/(Ni + Mo)—in the active component of the catalyst was 0.33.

The nickel, molybdenum, and boron oxide content in the catalysts was determined by inductively coupled plasma atomic emission spectrometry on a Varian 710-ES spectrometer (Agilent Technologies).

Catalytic Testing Procedure

The feedstock for the hydrodeoxygenation process was refined sunflower oil produced at MEZ Yug Rusi; the concentration of C_{16} and C_{18} acids was 6.4 and 92.5 wt %, respectively; the total content of unsaturated acids was 89.4 wt % [23].

Catalytic tests were conducted on a fixed-bed flow laboratory unit. Before testing, the catalysts were dried in a hydrogen stream (300 mL/min) at a temperature of 120°C for 5 h. The catalysts were sulfided in two stages at 230 and 340°C, a feed space velocity of 2 h^{-1}, and a hydrogen : feedstock ratio of 300 (STP)m^3 : m^3. A dimethyl disulfide solution in straight-run gasoline (0.6 wt % in terms of S) was used as a sulfiding agent.

Sunflower oil hydrodeoxygenation was run at a temperature of 380°C, a pressure of 4.0 MPa, a feed space velocity of 1 h^{-1}, and a hydrogen : oil ratio of 2500 nm^3 : m^3. Hydrogen sulfide was additionally batched into the reaction mixture in an amount of 0.4% of the amount of fed hydrogen.

Liquid and gaseous process products were separated in a separator at atmospheric pressure and 20°C. The composition of the gaseous products was determined in the on-line mode using a Khromos GKh-1000 dual-channel gas chromatograph. The inorganic components of the gas phase (H_2, H_2S, CO, CO_2, and H_2O) were analyzed using two 3 m × 4 mm packed columns coated with the Porapak R sorbent and activated carbon in combination with a thermal conductivity detector. The HC components of the gas phase (C_1–C_4, C_{5+}) were analyzed using a 60-m-long J&W DB-1 capillary column and a flame ionization detector. The HC composition of the stable liquid product was determined using a Khromos GKh-1000 gas chromatograph equipped with a 100-m-long Restek Rtx-1capillary column and a flame ionization detector. To determine the completeness of removal of oxygen and the group composition of the products, the liquid HC product was also analyzed by ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy (Bruker Avance 400, 400 MHz).

All catalyst samples were tested for 150 h. Sampling was conducted every 4 h during the first day and then every 24 h.

RESULTS AND DISCUSSION

Table 1 shows data on the actual content of nickel, molybdenum, and boron oxide (wt %) in the catalysts. It is evident from the data that the actual content of

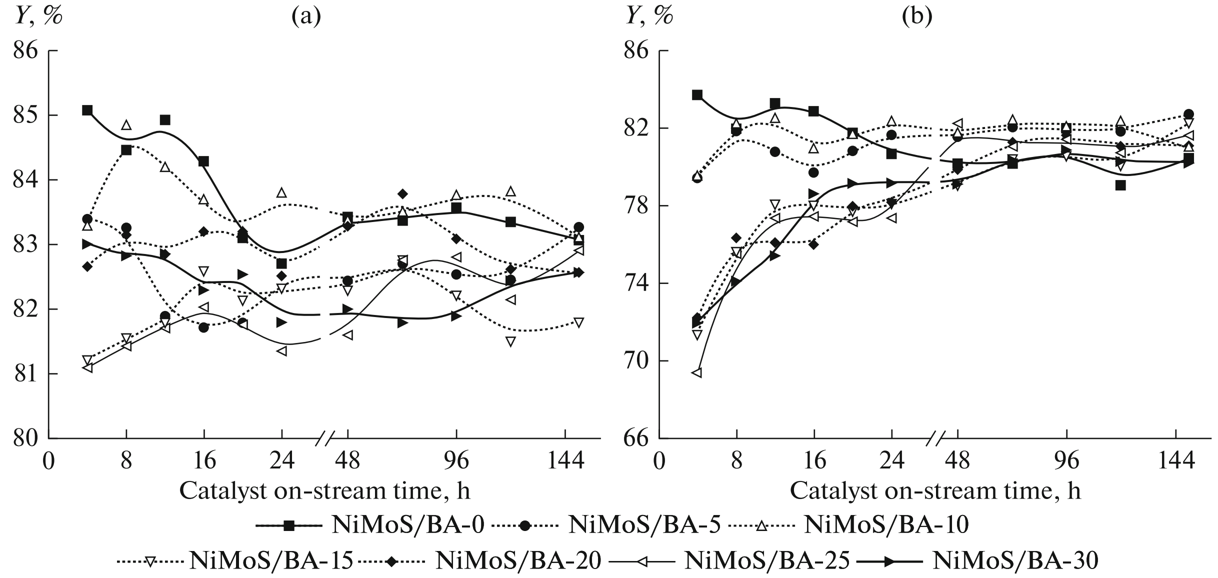

Fig. 1. Dependences of the yield (*Y*) of (a) liquid products and (b) C_{10+} hydrocarbons on the catalyst on-stream time for samples with a B_2O_3 content of 0–30 wt %.

nickel and molybdenum is close to the calculated value. The boron oxide content is slightly lower than the calculated value for the BA-30 sample; this fact can be attributed to the sublimation of B_2O_3 during the calcining of the support [25].

Analysis of the liquid process products by ^{1}H NMR spectroscopy showed that the spectra of all the products exhibit exclusively peaks with chemical shifts characteristic of aliphatic protons. Peaks with chemical shifts characteristic of protons present in oxygen-containing molecules and unsaturated or aromatic HCs were not detected in the spectra. Thus, it can be stated that all the tested catalysts provide the complete deoxygenation of the feedstock and the exhaustive hydrogenation of double bonds in the fatty acid residues of unsaturated acids contained in the oil.

The main products of sunflower oil conversion are C_{5+} liquid HCs, gaseous substances, and water. In the presence of all the catalysts, the liquid HC yield per fed oil (Fig. 1a) lies in a range of the theoretical yield, which, with allowance for the original oil composition, is 81% in the case of removal of entire oxygen in the form of CO and CO_2 and 86% in the case of removal of entire oxygen in the form of water. The catalysts with a boron oxide content of ≤10% provide a higher liquid product yield than that provided by the samples with a high modifier content. The effect is particularly pronounced in the first 24 h of testing, where the difference in the yields in the presence of the NiMoS/BA-0 and NiMoS/BA-30 samples can achieve 4%. This fact is attributed to the higher acidity of the catalysts with a boron oxide content of 15–30 wt % [26]. An increase in the acidity of the catalysts contributes to the occurrence of, first, decarboxylation/decarbonylation reactions owing to a decrease in the yield of C_{16} and C_{18} HCs [27, 28] and, second, the secondary cracking reactions of the resulting alkanes. Thus, Fig. 1b shows that, in the presence of the samples containing 15–30 wt % of boron oxide, the C_{10+} HC yield does not exceed 72–74% in the first hours of the test, while the yield of cracking products—C_5–C_9 HCs—can achieve 10–12%. With an increase in the catalyst on-stream time, the intensity of cracking reactions decreases, while the C_{10+} HC yield reaches a stationary level of 78–82% after the first day of testing. This “run-in period” of the catalyst is most probably associated with the deactivation of the strongest acid sites of the catalyst, which mediate the alkane cracking.

It should be noted that C_{21+} HCs are present in the composition of the products obtained in the presence of all the catalysts, although the feedstock does not contain fatty acids with the number of carbon atoms higher than 18. The maximum C_{21+} HC yield—3–3.5%—is observed in the presence of the NiMoS/Al_2O_3 sample; the yield remains almost unchanged throughout the entire test. In the presence of the samples with a higher acidity, namely, NiMoS/BA-25 and NiMoS/BA-30, the C_{21+} HC yield does not exceed 0.5% in the first hours of the test and increases to 1.5–2% at a catalyst on-stream time of more than 100 h. Most probably, the formation of these HCs is attributed to the fact that the feedstock initially contains oligomers of unsaturated fatty acids, which undergo hydrogenation and then cracking over the test catalyst samples.

The total yield of gaseous products (Figs. 2a, 2b) depends on the type of the selected support and

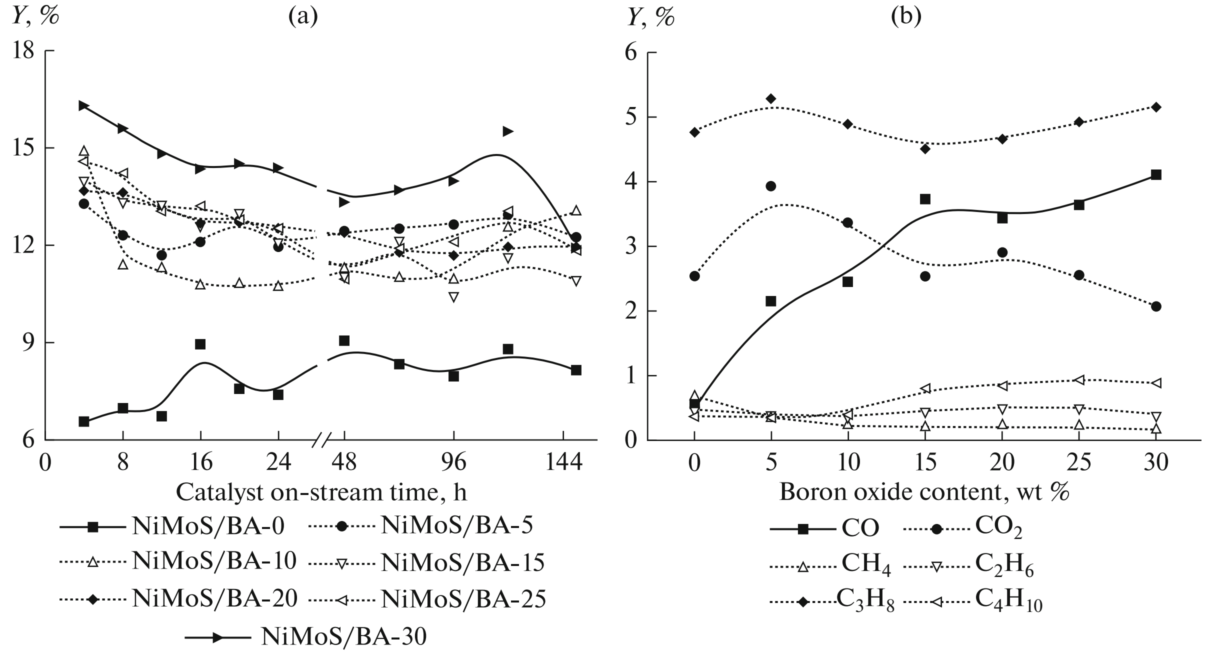

Fig. 2. (a) Dependence of the gas yield on the catalyst on-stream time for samples with a B_2O_3 content of 0–30 wt % and (b) dependence of the time-averaged gas composition on the B_2O_3 content in the catalysts.

increases with an increase in the acidity of the support. For the unmodified sample, it does not exceed 7–8%, whereas for the samples with a high acidity, which contain 25–30 wt % B_2O_3, the gas yield can achieve 15–16%. This parameter remains almost unchanged during the test. The time-averaged yield of the gas components—methane, ethane, propane, butane, CO, and CO_2—as a function of the boron oxide content is shown in Fig. 2b. It is evident from the figure that the propane yield is 4.7–5.0 wt % for all the samples; this value corresponds to the theoretical yield of 5.0 wt % that was calculated for the case of complete hydrogenation of all glycerol residues. Comparison of the propane yields and the total yield of liquid HCs showed that their molar ratio is 0.33 for all the catalysts; this value corresponds to the molar ratio of glycerol and fatty acid residues in oils. Thus, in the process, propane is formed exclusively via the hydrogenation of glycerol residues.

Under the test conditions, the following reactions can occur: the reduction of CO_2 to CO with hydrogen, the hydrogenation of CO and CO_2 to methane, and the oxidation of CO with water present in the reaction medium; therefore, the most correct method to determine the intensity of decarboxylation/decarbonylation reactions is to compare the total molar yield of the C_1 components and the molar yield of HCs with an odd number of carbon atoms. This ratio lies in a range of 0.95–1.1; it is close to the stoichiometric ratio; this fact suggests that the contribution of secondary reactions of hydrogenolysis and cracking of HCs to the formation of methane in the process is minimal. Concerning the ratio of the C_1 gas yields in the process, it can be stated that the methane yield does not exceed 0.5% and does not depend on the acidity of the sample. With an increase in the boron content in the samples, the carbon monoxide yield increases, while the CO_2 yield, conversely, decreases. Most probably, the ratio of the decarboxylation and decarbonylation reaction rates changes with a change in the acidity of the support; however, the causes of this effect have not yet apparently been described in the literature.

Figure 3a shows dependences of the isoalkane content in the products on the catalyst on-stream time for the tested set of samples. It is evident from the figure that, in the presence of the unmodified catalyst, the weight fraction of isoalkanes in the products does not exceed 12% in the initial period and decreases to 7–8% within 12 h. The introduction of boron oxide leads to a significant increase in the catalyst activity in the isomerization reaction. The content of branched alkanes in the product increases; for the samples with the maximum acidity of the support (at a B_2O_3 content of 20–30 wt %), it can achieve 77–78% in the initial period. However, as in the case of the unmodified catalyst, the isomerizing ability of the samples gradually decreases; after 150 h on stream, it does not exceed 25%. Thus, during the operation of the catalysts, the acid sites undergo deactivation.

The weight fraction of HCs with an odd number of carbon atoms in the products can be used to determine the ratio of rates of the deoxygenation reactions, in

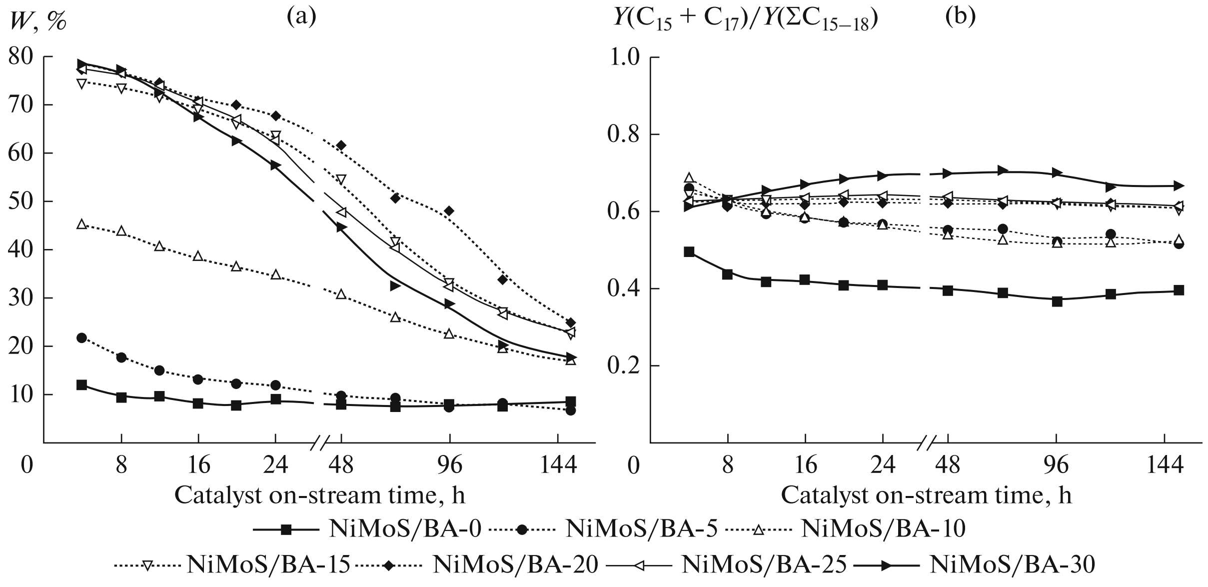

Fig. 3. Dependences of (a) the isoalkane content in the products and (b) the weight fraction of HCs with an odd number of carbon atoms in the C_{15-18} products on the catalyst on-stream time for samples with a B_2O_3 content of 0–30 wt %.

which oxygen is removed in the form of water, and the decarboxylation/decarbonylation reactions. It is evident from Fig. 3b that this parameter depends on the acidity of the support and increases from 0.4 for NiMoS/BA-0 to 0.7 for NiMoS/BA-30. These data are in good agreement with both the general decrease in the liquid product yield and the increase in the total gas yield and the total content of carbon oxides in the same set of catalysts. Thus, it can be stated that an increase in the catalyst acidity owing to the modification of the supports with boron oxide leads not only to an increase in the isomer content in the oil hydrodeoxygenation products, but also to an intensification of the decarbonylation/decarbonylation reactions.

The studies have revealed that sunflower oil hydrodeoxygenation at a temperature of 380°C, a pressure of 4 MPa, and a feed space velocity of 1 h^{-1} in the presence of $NiMoS/B_2O_3–Al_2O_3$ catalysts provides the formation of liquid HCs of the diesel fraction, which do not comprise sulfur- and oxygen-containing compounds, with a yield of 81–85%.

The introduction of 20–30 wt % of boron oxide into the oil hydrodeoxygenation catalysts makes it possible to obtain mixtures of diesel-fraction HCs with a weight fraction of isoalkanes in the products of up to 77–78%; however, the acid sites of the catalyst undergo deactivation during the first day on stream. At the same time, $NiMoS/B_2O_3–Al_2O_3$ catalysts are stable in hydrodeoxygenation reactions for at least 150 h.

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